PERFORMANCE SPECIFICATION 12A - SPECIFICATIONS AND TEST PROCEDURES FOR TOTAL VAPOR PHASE MERCURY CONTINUOUS EMISSION MONITORING SYSTEMS IN STATIONARY SOURCES

- 1.0 Scope and Application.
 - 1.1 Analyte.

<u> Analyte</u>	CAS No.			
Mercury (Hg)	7439-97-6			

- 1.2 Applicability.
- 1.2.1 This specification is for evaluating the acceptability of total vapor phase Hg continuous emission monitoring systems (CEMSs) installed on the exit gases from fossil fuel fired boilers at the time of or soon after installation and whenever specified in the regulations. The Hg CEMS must be capable of measuring the total concentration in $\mu g/m^3$ (regardless of speciation) of vapor phase Hg, and recording that concentration on a dry basis, corrected to 20 degrees C and 7% CO₂. Particle bound Hg is not included. The CEMS must include a) a diluent (CO₂) monitor, which must meet Performance Specification 3, and b) an automatic sampling system. Existing diluent and flow monitoring equipment can be used.

This specification is not designed to evaluate an installed CEMS's performance over an extended period of time nor does it identify specific calibration techniques and auxiliary procedures to assess the CEMS's performance. The source owner or operator,

however, is responsible to calibrate, maintain, and operate the CEMS properly. The Administrator may require, under Section 114 of the Act, the operator to conduct CEMS performance evaluations at other times besides the initial test to evaluate the CEMS performance. See 40 CFR Part 60, Sect.60.13(c).

2.0 Summary of Performance Specification

Procedures for measuring CEMS relative accuracy, measurement error and drift are outlined. CEMS installation and measurement location specifications, and data reduction procedures are included. Conformance of the CEMS with the Performance Specification is determined.

3.0 Definitions

- 3.1 Continuous Emission Monitoring System (CEMS) means the total equipment required for the determination of a pollutant concentration. The system consists of the following major subsystems:
- 3.2 Sample Interface means that portion of the CEMS used for one or more of the following: sample acquisition, sample transport, sample conditioning, and protection of the monitor from the effects of the stack effluent.
- 3.3 Hg Analyzer means that portion of the CEMS that measures the total vapor phase Hg mass concentration and generates a proportional output.
- 3.4 Diluent Analyzer (if applicable) means that portion of the CEMS that senses the diluent gas (CO_2) and generates an

output proportional to the gas concentration.

- 3.5 Data Recorder means that portion of the CEMS that provides a permanent electronic record of the analyzer output. The data recorder can provide automatic data reduction and CEMS control capabilities.
- 3.6 Span Value means the upper limit of the intended Hg concentration measurement range. The span value is a value equal to two times the emission standard.
- 3.7 Measurement Error (ME) means the difference between the concentration indicated by the CEMS and the known concentration generated by a reference gas when the entire CEMS, including the sampling interface, is challenged. A ME test procedure is performed to document the accuracy and linearity of the CEMS at several points over the measurement range.
- 3.8 Upscale Drift (UD) means the difference in the CEMS output responses to a Hg reference gas when the entire CEMS, including the sampling interface, is challenged after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.
- 3.9 Zero Drift (ZD) means the difference in the CEMS output responses to a zero gas when the entire CEMS, including the sampling interface, is challenged after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.
 - 3.10 Relative Accuracy (RA) means the absolute mean

difference between the pollutant concentration(s) determined by the CEMS and the value determined by the reference method (RM) plus the 2.5 percent error confidence coefficient of a series of tests divided by the mean of the RM tests or the applicable emission limit.

- 4.0 Interferences. [Reserved]
- 5.0 Safety.

The procedures required under this performance specification may involve hazardous materials, operations, and equipment. This performance specification may not address all of the safety problems associated with these procedures. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicable regulatory limitations prior to performing these procedures. The CEMS user's manual and materials recommended by the reference method should be consulted for specific precautions to be taken.

- 6.0 Equipment and Supplies.
 - 6.1 CEMS Equipment Specifications.
- 6.1.1 Data Recorder Scale. The CEMS data recorder output range must include zero and a high level value. The high level value must be approximately 2 times the Hg concentration corresponding to the emission standard level for the stack gas under the circumstances existing as the stack gas is sampled. If a lower high level value is used, the CEMS must have the capability of providing multiple high level values (one of which

is equal to the span value) or be capable of automatically changing the high level value as required (up to specified high level value) such that the measured value does not exceed 95 percent of the high level value.

- 6.1.2 The CEMS design should also provide for the determination of response drift at both the zero and mid-level value. If this is not possible or practical, the design must allow these determinations to be conducted at a low-level value (zero to 20 percent of the high-level value) and at a value between 50 and 100 percent of the high-level value.
- 6.2 Reference Gas Delivery System. The reference gas delivery system must be designed so that the flowrate of reference gas introduced to the CEMS is the same at all three challenge levels specified in Section 7.1 and at all times exceeds the flow requirements of the CEMS.
- 6.3 Other equipment and supplies, as needed by the applicable reference method used. See Section 8.6.2.
- 7.0 Reagents and Standards.
 - 7.1 Reference Gases.
 - 7.1.1 Zero N2 or Air. Less than 0.1 μ g Hg/m³.
 - 7.1.2 Mid-Level Hg^0 and $HgCl_2$. 40% to 60% of span.
 - 7.1.3 High-Level Hg^0 and $HgCl_2$ 80% to 100% of span.
- 7.2 Reagents and Standards. May be required for the reference methods. See Section 8.6.2.
- 8.0 Performance Specification Test Procedure.

- 8.1 Installation and Measurement Location Specifications.
- $8.1.1\,$ CEMS Installation. Install the CEMS at an accessible location downstream of all pollution control equipment. Since the Hg CEMS sample system normally extracts gas from a single point in the stack, use a location that has been shown to be free of stratification for SO_2 and NO_x through concentration measurement traverses for those gases. If the cause of failure to meet the RA test requirement is determined to be the measurement location and a satisfactory correction technique cannot be established, the Administrator may require the CEMS to be relocated.

Measurement locations and points or paths that are most likely to provide data that will meet the RA requirements are listed below.

- 8.1.1 Measurement Location. The measurement location should be (1) at least eight equivalent diameters downstream of the nearest control device, point of pollutant generation, bend, or other point at which a change of pollutant concentration or flow disturbance may occur and (2) at least two equivalent diameters upstream from the effluent exhaust. The equivalent duct diameter is calculated as per 40 CFR part 60, Appendix A, Method 1.
- 8.1.2 Hg CEMS Sample extraction Point. Use a sample extraction point (1) no less than 1.0 meter from the stack or duct wall, or (2) within the centroidal velocity traverse area of

the stack or duct cross section.

- 8.2 Reference Method (RM) Measurement Location and Traverse Points. The RM measurement location should be at a point or points in the same stack cross sectional area as the CEMS is located, according to the criteria above. The RM and CEMS locations need not be immediately adjacent. They should be as close as possible without causing interference with one another.
- 8.3 Measurement Error (ME) Test Procedure. The Hg CEMS must be constructed to permit the introduction of known (NIST traceable) concentrations of elemental mercury (Hg°) and mercuric chloride (HgCl₂) separately into the sampling system of the CEMS immediately preceding the sample extraction filtration system such that the entire CEMS can be challenged. Inject sequentially each of the three reference gases (zero, mid-level, and high level) for each Hg species. CEMS measurements of each reference gas shall not differ from their respective reference values by more than 5% of the span value. If this specification is not met, identify and correct the problem before proceeding.
 - 8.4 Upscale Drift (UD) Test Procedure.
- 8.4.1 UD Test Period. While the affected facility is operating at more than 50 percent of normal load, or as specified in an applicable subpart, determine the magnitude of the UD once each day (at 24-hour intervals) for seven consecutive days according to the procedure given in Sections 8.4.2 through 8.4.3.
 - 8.4.2 The purpose of the UD measurement is to verify the

ability of the CEMS to conform to the established CEMS response used for determining emission concentrations or emission rates. Therefore, if periodic automatic or manual adjustments are made to the CEMS zero and response settings, conduct the UD test immediately before these adjustments, or conduct it in such a way that the UD can be determined.

- 8.4.3 Conduct the UD test at the mid-level point specified in Section 7.1. Evaluate upscale drift for elemental Hg (Hg°) only. Introduce the reference gas to the CEMS. Record the CEMS response and subtract the reference value from the CEM value(see example data sheet in Figure 12A-1).
 - 8.5 Zero Drift (ZD) Test Procedure.
- 8.5.1 ZD Test Period. While the affected facility is operating at more than 50 percent of normal load, or as specified in an applicable subpart, determine the magnitude of the ZD once each day (at 24-hour intervals) for seven consecutive days according to the procedure given in Sections 8.5.2 through 8.5.3.
- 8.5.2 The purpose of the ZD measurement is to verify the ability of the CEMS to conform to the established CEMS response used for determining emission concentrations or emission rates. Therefore, if periodic automatic or manual adjustments are made to the CEMS zero and response settings, conduct the ZD test immediately before these adjustments, or conduct it in such a way that the ZD can be determined.
 - 8.5.3 Conduct the ZD test at the zero level specified in

- Section 7.1. Introduce the zero gas to the CEMS. Record the CEMS response and subtract the zero value from the CEM value (see example data sheet in Figure 12A-1).
 - 8.6 Relative Accuracy (RA) Test Procedure.
- 8.6.1 RA Test Period. Conduct the RA test according to the procedure given in Sections 8.6.2 through 8.6.6 while the affected facility is operating at normal full load, or as specified in an applicable subpart. The RA test can be conducted during the UD test period.
- 8.6.2 Reference Method (RM). Unless otherwise specified in an applicable subpart of the regulations, use either Method 29 in Appendix A to 40 CFR Part 60, or ASTM Method D 6784-02 (incorporated by reference in §60.17) as the RM for Hg. Do not include the filterable portion of the sample when making comparisons to the CEMS results. Conduct all RM tests with paired or duplicate sampling systems.
- 8.6.3 Sampling Strategy for RM Tests. Conduct the RM tests in such a way that they will yield results representative of the emissions from the source and can be compared to the CEMS data. It is preferable to conduct the diluent (if applicable), moisture (if needed), and Hg measurements simultaneously. However, diluent and moisture measurements that are taken within an hour of the Hg measurements can used to adjust the results to a consistent basis. In order to correlate the CEMS and RM data properly, note the beginning and end of each RM test period for

each paired RM run (including the exact time of day) on the CEMS chart recordings or other permanent record of output.

8.6.4 Number and length of RM Tests. Conduct a minimum of nine paired sets of all necessary RM test runs that meet the relative standard deviation criteria of this PS. Use a minimum sample run time of 2 hours for each pair.

NOTE: More than nine paired sets of RM tests can be performed. If this option is chosen, test results can be rejected so long as the total number of paired RM test results used to determine the CEMS RA is greater than or equal to nine. However, all data must be reported, including the rejected data.

- 8.6.5 Correlation of RM and CEMS Data. Correlate the CEMS and the RM test data as to the time and duration by first determining from the CEMS final output (the one used for reporting) the integrated average pollutant concentration or emission rate for each pollutant RM test period. Consider system response time, if important, and confirm that the results are on a consistent moisture, temperature, and diluent concentration basis with the paired RM test. Then, compare each integrated CEMS value against the corresponding average of the paired RM values.
 - 8.6.6 Paired RM Outliers.
- a. Outliers are identified through the determination of precision and any systematic bias of the paired RM tests. Data that do not meet this criteria should be flagged as a data

quality problem. The primary reason for performing dual RM sampling is to generate information to quantify the precision of the RM data. The relative standard deviation (RSD) of paired data is the parameter used to quantify data precision. Determine RSD for two simultaneously gathered data points as follows:

$$RSD = 100\% * \left| \left(Ca - Cb \right) \right| / \left(Ca + Cb \right)$$
 Eq. 12A-1

where Ca and Cb are concentration values determined from trains A and B respectively. For RSD calculation, the concentration units are unimportant so long as they are consistent.

- b. A minimum precision criteria for RM Hg data is that RSD for any data pair must be $\leq 10\%$ as long as the mean Hg concentration is greater than 1.0 $\mu g/m^3$. If the mean Hg concentration is less than or equal to 1.0 $\mu g/m^3$, the RSD must be $\leq 20\%$. Pairs of RM data exceeding these RSD criteria should be eliminated from the data set used to develop a Hg CEMS correlation or to assess CEMS RA.
- 8.6.7 Calculate the mean difference between the RM and CEMS values in the units of the emission standard, the standard deviation, the confidence coefficient, and the RA according to the procedures in Section 12.0.
- 8.7 Reporting. At a minimum (check with the appropriate EPA Regional Office, State, or Local Agency for additional requirements, if any), summarize in tabular form the results of the RD tests and the RA tests or alternative RA procedure, as

appropriate. Include all data sheets, calculations, charts (records of CEMS responses), reference gas concentration certifications, and any other information necessary to confirm that the performance of the CEMS meets the performance criteria.

- 9.0 Quality Control. [Reserved]
- 10.0 Calibration and Standardization. [Reserved]
- 11.0 Analytical Procedure.

Sample collection and analysis are concurrent for this Performance Specification (see Section 8.0). Refer to the RM employed for specific analytical procedures.

12.0 Calculations and Data Analysis.

Summarize the results on a data sheet similar to that shown in Figure 2-2 for Performance Specification 2.

- 12.1 Consistent Basis. All data from the RM and CEMS must be on a consistent dry basis and, as applicable, on a consistent diluent basis. Correct the RM and CEMS data for moisture and diluent as follows:
- 12.1.1 Moisture Correction (as applicable). Correct each wet RM run for moisture with the corresponding Method 4 data; correct each wet CEMS run using the corresponding CEMS moisture monitor date using Equation 12A-2.

Concentration_(dry) =
$$\frac{\text{Concentration}_{\text{(wet)}}}{(1-B_{ws})}$$
 Eq. 12A-2

12.1.2 Correction to Units of Standard (as applicable).

Correct each dry RM run to the units of the emission standard with the corresponding Method 3B data; correct each dry CEMS run using the corresponding CEMS diluent monitor data as follows:

12.1.2.1 Correct to Diluent Basis. The following is an example of concentration (ppm) correction to 7% oxygen.

$$ppm_{(corr)} = ppm_{(uncorr)} \left[\frac{20.9 - 7.0}{20.9 - %O_{2(dry)}} \right]$$
 Eq. 12A-3

The following is an example of mass/gross calorific value (lbs/million Btu) correction.

lbs/MMBtu = $Conc_{(dry)}$ (F-factor) (20.9/20.9- $%0_2$)

12.2 Arithmetic Mean. Calculate the arithmetic mean of the difference, d, of a data set as follows:

$$\overline{d} = \frac{1}{n} \sum_{i=1}^{n} d_i$$
 Eq. 12A-4

where:

n = Number of data points.

12.3 Standard Deviation. Calculate the standard deviation, $S_{\rm d}$, as follows:

$$S_{d} = \begin{bmatrix} \sum_{i=1}^{n} d_{i}^{2} - \frac{\left[\sum_{i=1}^{n} d_{i}\right]^{2}}{\sum_{i=1}^{n} n} \end{bmatrix}^{\frac{1}{2}}$$
Eq. 12A-5

where:

 $\sum_{i=1}^{n} d_{i} = Algebraic summation of the individual differences d_{i}.$

12.4 Confidence Coefficient. Calculate the 2.5 percent error confidence coefficient (one-tailed), CC, as follows:

CC =
$$t_{0.975} \frac{S_d}{\sqrt{n}}$$
 Eq. 12A-6

12.5 Relative Accuracy. Calculate the RA of a set of data as follows:

$$RA = \frac{[|\overline{d}| + |CC|]}{\overline{RM}} \times 100$$
 Eq. 12A-7

where:

- |d| = Absolute value of the mean differences (from Equation 12A-4).
- |CC| = Absolute value of the confidence coefficient (from Equation 12A-6).

standard value in the denominator of Eq. 12A-7 in place of RM. In all other cases, use RM.

13.0 Method Performance.

- 13.1 Measurement Error (ME). ME is assessed at mid-level and high-level values as given below using standards for both Hg° and HgCl_2 . The mean difference between the indicated CEMS concentration and the reference concentration value for each standard shall be no greater than 5% of span. The same difference for the zero reference gas shall be no greater than 5% of span.
- 13.2 Upscale Drift (UD). The CEMS design must allow the determination of UD of the analyzer. The CEMS response can not drift or deviate from the benchmark value of the reference standard by more than 5% of span for the mid level value. Evaluate upscale drift for elemental Hg (Hg^o) only.
- 13.3 Zero Drift (ZD). The CEMS design must allow the determination of drift at the zero level. This drift shall not exceed 5% of span.
- 13.4 Relative Accuracy (RA). The RA of the CEMS must be no greater than 20 percent of the mean value of the RM test data in terms of units of the emission standard, or 10 percent of the applicable standard, whichever is greater.
- 14.0 Pollution Prevention. [Reserved]
- 15.0 Waste Management. [Reserved]
- 16.0 Alternative Procedures. [Reserved]

17.0 Bibliography.

- 17.1 40 CFR Part 60, Appendix B, "Performance Specification 2 Specifications and Test Procedures for SO_2 and NO_X Continuous Emission Monitoring Systems in Stationary Sources".
- 17.2 40 CFR Part 60, Appendix A, "Method 29 Determination of Metals Emissions from Stationary Sources".
- 17.3 ASTM Method D6784-02, "Standard Test Method for Elemental, Oxidized, Particle-Bound and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method)".
- 18.0 Tables and Figures.

TABLE 12A-1. t-VALUES.

n ^a	t _{0.975}	nª	t _{0.975}	nª	t _{0.975}
2	12.706	7	2.447	12	2.201
3	4.303	8	2.365	13	2.179
4	3.182	9	2.306	14	2.160
5	2.776	10	2.262	15	2.145
6	2.571	11	2.228	16	2.131

The values in this table are already corrected for n-1 degrees of freedom.

Use n equal to the number of individual values.

		Date	Reference	CEMS	Measurement	Drift
	Day	and	Value	Value	Error	
		Time	(C)	(M)		
Zero						
Level						
Mid-						
level						
ievei						
II de la						
High-						
level						

Figure 12A-1. Zero and Upscale Drift Determination.